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# Accuracy of Pesticide Reference Standard Solutions. Part II. Chemical Stability Under Four Storage Conditions

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16. ABSTRACT

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# Accuracy of Pesticide Reference Standard Solutions. Part II. Chemical Stability Under Four Storage Conditions

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**A study was undertaken to assess the long-term chemical stability of dilute standard pesticide solutions of 4 compound classes. The solutions were studied under 4 storage conditions: freezer at −15°C; refrigerator at 3°C; ambient temperature in the dark; and ambient temperature on the bench top exposed to fluorescent and natural light. Pesticide compounds including 27 organochlorines, 20 organophosphates, 10 triazines, and 13 carbamates were monitored for periods of 6 months to 2 years. Most of the compounds were stable (<10% decomposition) under all conditions for the full length of the study. Solutions of CDEC, butylate, and disulfoton, however, decomposed when stored under all storage conditions. Solutions of carbaryl, methiocarb, and carbofuran decomposed when stored at ambient laboratory temperature with exposure to light. Recommendations are made for formulating solvents, storage, and practical shelf life of high concentration stock solutions and dilute gas chromatographic working standards representing 4 pesticide classes.**

A careful consideration of the integrity of standard solutions is of utmost importance to any analytical laboratory. Pesticide residue chemists are generally concerned with the concentration accuracy and chemical stability of their reference solutions. However, laboratory time and resources are rarely available for conducting the long-term studies necessary to evaluate procedures for preparation, storage maintenance, and use of standard solutions.

Suett et al. (1) reported on a 2-year evaluation of the storage stability of 6 pesticides after our study had been completed. The compounds were formulated in 3 solvents at 1 mg/mL, sealed in ampules, and stored in the dark at −20, 1, and 20°C. The study concluded that these concentrated stock solutions were at least as stable as the pure primary standards from which they were prepared.

A reference standard solution stability study was also reported by the Food and Drug Administration (2) for 7 common organochlorine pesticides. Materials were formulated in isooctane and stored in Pyrex volumetric flasks at ambient temperature with exposure to fluorescent lamps. It was concluded that no qualitative changes occurred in the dilute solutions during the 8-month testing period. The experiment was not designed to monitor changes in concentration.

Investigations were conducted by this quality assurance coordinating laboratory, which resulted in a 2-part report of the various factors affecting the analytical integrity of standard solutions representing 4 pesticide classes. The first study (3) concerned the effect of the choice of solvent, solution container, and storage conditions on the evaporation of the solvent and the resultant changes of the standard solution concentration.

The present report describes studies undertaken to assess the long-term chemical stability of standard reference materials which have been formulated in appropriate organic solvents and stored under various conditions. This study encompasses 2 areas of investigation. The first is an evaluation of chemical stability of dilute gas chromatographic (GC) standard reference solutions (working solutions) of organochlorine, organophosphate, carbamate, and triazine pesticides in solvents suitable for dissolution of the compounds and also compatible with the GC detector systems. The second and similar evaluation was conducted on acetone solutions of organochlorine and organophosphate pesticides formulated for use as fortification solutions in our quality assurance program for water and blood serum analyses.

These 2 stability studies were intended to identify compounds that are not stable in solution, and to evaluate the magnitude of the instability under normal residue laboratory conditions. No effort was made to rigorously control the temperatures, evaluate the total amount of light radiation absorbed by the test solutions, or in any other way to make this a rigorous physical-chemical study. The figures presented in this paper are presented as representations of the data trend. They are not intended to be

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studied in great detail to establish the degradation curve of each specific compound.

## Experimental

### *Reagents and Materials*

(a) *Solvents.*—Isooctane (2,2,4-trimethylpentane), hexane, toluene, ethyl acetate, and acetone; all distilled-in-glass quality (Burdick & Jackson Laboratories, Inc., Muskegon, MI 49442).

(b) *Analytical standards.*—Obtained from the Pesticides Analytical Standards Repository, Environmental Protection Agency, Research Triangle Park, NC 27711. (1) *Organochlorines.*—Aldrin (99.5%), Aroclor 1016, Aroclor 1254, β-BHC (99.8%), technical chlordane, chlordecone (87.3%), chlordene (99.6%), DCPA (99.9%), *p,p'*-DDD (99+%), *p,p'*-DDE (99%), *o,p'*-DDT (99+%), *p,p'*-DDT (99+%), dieldrin (99.9%), endosulfan I (100%), endosulfan II (100%), endrin (99.0%), hexachlorobenzene (98+%), heptachlor (99.8%), heptachlor epoxide (99.3%), 1-hydroxychlordene (100%), lindane (99.9%), methoxychlor (99+%), mirex (99.9%), *trans*-nonachlor (100%), oxychlordane (98%), PCNB (99.03%), and toxaphene (68.9% Cl).

(2) *Organophosphates.*—Azinphos methyl (99.5%), carbophenothion (98.5%), chlorpyrifos (99%), DEF (94.6%), dichlofenthion (97.0%), dimethoate (99.5%), dioxathion (74%), disulfoton (98.8%), ethion (95.5%), ethoprop (99%), fenthion (98.2%), leptophos (100%), malathion (99.3%), methyl parathion (99+%), mevinphos (64.5%), parathion (99+%), phencapton (98.5%), phorate (99.9%), phosmet (99.5%), and ronnel (99+%).

(3) *Carbamates.*—Aminocarb (97.0%), bufencarb (97.8%), butylate (99.7%), carbaryl (99.7%), carbofuran (99.5%), CDEC (98.6%), mecarbam (99.6%), methiocarb (99.0%), mexacarbate (99%), pirimicarb (100%), promecarb (>98%), propoxur (98.4%), and thiobencarb (99.9%)

(4) *Triazines.*—Ametryn (99+%), atraton (89+%), atrazine (99+%), cyanazine (99%), cyprazine (99.3%), prometon (99.5%), prometryn (99+%), propazine (99+%), simazine (99+%), and terbutryn (98+%).

(c) *Standard prescription bottles.*—Clear glass, screw-cap, 2 oz and ½ oz (Brockway Glass Co. Inc., Brockway, PA).

(d) *Teflon cap liners.*—For prescription bottles (A. H. Thomas, Philadelphia, PA; Cat. No. 2390-H).

(e) *Gas chromatographs.*—(1) Tracor Model 222 equipped with $^{63}$Ni electron capture detectors (ECD) operated in the DC mode and dual flame photometric detector (FPD); 1.8 m × 4 mm id glass columns for ECD packed with 1.5% OV-17/1.95% OV-210 on 80–100 mesh Gas-Chrom Q; 1.8 m × 4 mm id glass column for FPD packed with 4% SE-30/6% OV-210 on 80–100 mesh Gas-Chrom Q; oven 190–200°C; injector and transfer line 250°C; column nitrogen flow 60 mL/min; FPD gases 50 mL hydrogen/min and 100 mL air/min.

(2) Hewlett-Packard Model 5710 equipped with N/P thermionic detectors (NPD); 1.8 m × 4 mm id glass column packed with 5% OV-101 on 100–120 mesh Carbowax 20M support-bonded on Chromosorb WAW (4, 5); oven 180–200°C; injector 200°C; detector 300°C; detector gas flows, 3 mL hydrogen and 50 mL air/min; column gas flow 60 mL helium/min.

### *Experimental Procedure*

The following definitions apply for this experiment:

Primary standard: the pure standard compound as received from the Standards Repository.

Stock solutions: solutions of individual compounds (concentration >100 μg/mL) prepared directly from primary standards, used to prepare solutions of individual compounds or mixtures at appropriate injection concentrations, and used as a reference point in the experiment.

Working solutions: solutions at the concentration appropriate for injection (ECD <100 pg/μL, FPD and NPD between 100 pg/μL and 10 ng/μL) and tested in this experiment.

In this experiment, one month is defined as 28 days.

All quantitations were done by manual peak height measurement.

### *Reference Stock Solution Preparation and Storage for Both Studies*

On the first day of the experiment, reference stock solutions were prepared from the respective primary standards at approximately 200 μg/mL. The stock solutions of the organochlorines and organophosphates were prepared in benzene. Carbamate stock solutions were prepared in toluene. Stock solutions of triazines were prepared in ethyl acetate because of insolubility in toluene and benzene. All stock solutions were stored in the freezer at −15°C when not in use.

### *Preparation, Storage, and Stability Testing of Dilute Working Solutions*

*Organochlorines and organophosphates (in isooc-*

Table 1. Organochlorine and organophosphate isooctane solutions and 2-year stability test results

| Compound | Soln[a] | Concn, pg/μL | Degradation at storage condition[b] | | | |
|---|---|---|---|---|---|---|
| | | | Freezer −15°C | Refrig. +3°C | Dark ~24°C | Light ~24°C |
| **Organochlorines** | | | | | | |
| Aldrin | B | 9.9 | + | + | + | + |
| Aroclor 1016 | E | 100 | + | + | + | + |
| Aroclor 1254 | F | 200 | + | + | + | + |
| β-BHC | C | 16.2 | + | + | + | + |
| γ-BHC (lindane) | C | 6.0 | + | + | + | + |
| Chlordane (tech) | G | 80.4 | + | + | + | + |
| Chlordecone[c] | K | 19.5 | + | + | + | + |
| Chlordene | D | 5.3 | + | + | + | + |
| DCPA | B | 15.1 | + | + | + | + |
| *p,p'*-DDD | B | 30.2 | + | + | + | + |
| *p,p'*-DDE | A | 22.0 | + | + | + | + |
| *o,p'*-DDT | A | 36.5 | + | + | + | + |
| *p,p'*-DDT | A | 47.8 | + | + | + | + |
| Dieldrin | B | 20.6 | + | + | + | + |
| Endosulfan I | C | 26.0 | + | + | + | + |
| Endosulfan II | C | 30.0 | + | + | + | + |
| Endrin | C | 50.0 | + | + | + | + |
| HCB | C | 5.0 | + | + | + | + |
| Heptachlor | A | 8.9 | + | + | + | + |
| Heptachlor epoxide | A | 15.0 | + | + | + | + |
| 1-Hydroxychlordene | D | 15.8 | + | + | + | + |
| Methoxychlor | F | 71.4 | + | + | + | + |
| Mirex | A | 48.3 | + | + | + | + |
| *trans*-Nonachlor | D | 14.0 | + | + | + | + |
| Oxychlordane | D | 13.7 | + | + | + | + |
| PCNB | A | 7.8 | + | + | + | + |
| Toxaphene | H | 452 | + | + | + | + |
| **Organophosphates** | | | | | | |
| Azinphos methyl | J | 2500 | + | + | + | + |
| Carbophenothion | J | 400 | + | + | + | + |
| Chlorpyrifos | J | 150 | + | + | + | + |
| DEF | J | 300 | + | + | + | + |
| Dichlofenthion | K | 100 | + | + | + | + |
| Dimethoate | L | 100 | + | + | + | + |
| Dioxathion | L | 300 | + | + | + | + |
| Disulfoton | J | 75 | −(13.8%) | + | −(34.2%) | −(68.8%) |
| Ethion | K | 150 | + | + | + | + |
| Ethoprop | L | 50 | + | + | + | + |
| Ethyl parathion | K | 150 | + | + | + | + |
| Fenthion | L | 100 | + | + | + | + |
| Leptophos | K | 850 | + | + | + | + |
| Malathion | L | 200 | + | + | + | + |
| Methyl parathion | K | 100 | + | + | + | + |
| Mevinphos | L | 100 | + | + | + | + |
| Phencapton | K | 130 | + | + | + | + |
| Phorate | J | 50 | + | + | + | + |
| Phosmet | J | 1250 | + | + | + | + |
| Ronnel | K | 100 | + | + | + | + |

[a] Identifies components of pesticide mixtures.
[b] Stable (+) or unstable (−) and % decomposition.
[c] Solvent 1% methanol in benzene because of electron capture response characteristics (4).

*tane*).—To reduce the number of necessary GC injections, mixtures of structurally similar standards were prepared by dilution to appropriate injection level concentrations. The mixture compositions and concentrations are specified in Table 1. Each injection concentration working standard solution was divided into three ½ oz prescription bottles with Teflon-lined caps and stored as follows: (1) one in the freezer (−15°C) for one year; (2) one in the refrigerator (+3°C) for one year; and (3) one at ambient laboratory temperature (ca 25°C) stored in the cabinet under the laboratory bench without exposure to light for one year, followed by storage at

Table 2. Carbamate toluene solutions and triazine ethyl acetate solutions and 1-year stability test results

| Compound | Concn, pg/μL | Degradation at storage condition[a] | | | |
|---|---|---|---|---|---|
| | | Freezer −15°C | Refrig. +3°C | Dark ~24°C | Light ~24°C |
| **Carbamates (in Toluene)** | | | | | |
| Aminocarb | 200 | + | + | + | + |
| Bufencarb | 800 | + | + | + | + |
| Butylate | 200 | −(51%) | −(51%) | −(51%) | −(49%) |
| Carbaryl | 1600 | + | + | + | −(38%) |
| Carbofuran | 400 | + | + | + | −(17%) |
| CDEC | 30 | −(65%) | −(59%) | −(47%) | −(98%) |
| Mecarbam | 100 | + | + | + | + |
| Methiocarb | 400 | + | + | −(13%) | −(40%) |
| Mexacarbate | 300 | + | + | + | + |
| Pirimicarb | 120 | + | + | + | + |
| Promecarb | 400 | + | + | + | + |
| Propoxur | 200 | + | + | + | + |
| Thiobencarb | 400 | + | + | + | + |
| **Triazines (in Ethyl Acetate)** | | | | | |
| Ametryn | 400 | + | + | + | −(17%) |
| Atraton | 200 | + | + | −(14%) | +[b] |
| Atrazine | 200 | + | + | −(50%) | −(13%) |
| Cyanazine | 500 | + | + | + | + |
| Cyprazine | 200 | + | + | + | + |
| Prometon | 200 | + | + | + | −(11%) |
| Prometryn | 300 | + | + | + | −(11%) |
| Propazine | 200 | + | + | + | + |
| Simazine | 200 | + | + | + | + |
| Terbutryn | 400 | + | + | + | + |

[a] Stable (+) or unstable (−) and % decomposition.
[b] Reference to discussion, this solution concentrated.

ambient temperature on the laboratory bench exposed to fluorescent and natural light for another year.

The 3 storage test solutions were compared with fresh dilutions of the respective reference stock solutions monthly (28 days) to monitor for changes in the concentration of any of the compounds and to watch for the appearance of any decomposition products. The test solutions and the fresh reference standard solutions were always injected in duplicate.

Fresh re-weighed reference stock solutions of each compound were prepared every 3–4 months from the original primary standard used on day 1. After establishing that the new reference standard solutions agreed within 3% of old reference standard solutions, the older reference solutions were discarded. All analyses of the respective organochlorine and organophosphate mixtures were made on the Tracor 222 gas chromatograph. The electron capture detector was used for the organochlorines and the flame photometric detector (P mode) was used for the organophosphates.

*Carbamates (in toluene) and triazines (in ethyl acetate).*—The experimental design was identical to that of the organochlorines and organophosphates with 2 modifications. Because of smaller numbers of compounds in these 2 groups and suspected catalytic breakdown of carbamates in solution as mixtures (R. Moseman, Environmental Protection Agency, Research Triangle Park, NC; February 1975), these test solutions were formulated individually. Three samples of each test solution in ½ oz prescription bottles were prepared and stored at the same conditions used for organochlorines and organophosphates. A fourth test solution was stored at ambient temperature exposed to light. Table 2 lists the compounds tested and their respective solution concentrations.

All GC analyses of these 2 classes were made on the Hewlett-Packard 5710 gas chromatograph equipped with N/P thermionic detectors. The modified Carbowax 20M support-bonded column packings (4, 5) were used because of their vastly improved chromatography of carbamate compounds (6).

Table 3. Organochlorine and organophosphate acetone solutions and half-year stability test results

| Compound | Soln[a] | Concn, pg/μL | Degradation at storage condition[b] | | | |
|---|---|---|---|---|---|---|
| | | | Freezer −15°C | Refrig. +3°C | Dark ~24°C | Light ~24°C |
| **Organochlorines** | | | | | | |
| Aldrin | N | 100 | + | + | + | + |
| Aroclor 1016 | O | 1000 | + | + | + | + |
| Aroclor 1254 | P | 2000 | + | + | + | + |
| β-BHC | M | 160 | + | + | + | + |
| Chlordane (tech) | Q | 805 | + | + | + | + |
| p,p'-DDE | M | 220 | + | + | + | + |
| p,p'-DDT | M | 475 | + | + | + | + |
| Dieldrin | N | 200 | + | + | + | + |
| Endrin | M | 660 | + | + | + | + |
| HCB | M | 50 | + | + | + | + |
| Heptachlor | N | 90 | + | + | + | + |
| Heptachlor epoxide | N | 150 | + | + | + | + |
| 1-Hydroxychlordene | N | 150 | + | + | + | + |
| **Organophosphates** | | | | | | |
| Carbophenothion | R | 4000 | + | + | + | + |
| Chlorpyrifos | R | 2000 | + | + | + | + |
| Dichlofenthion | R | 1000 | + | + | + | + |
| Dimethoate | T | 5000 | + | + | + | + |
| Ethion | S | 2500 | + | + | + | + |
| Ethyl parathion | R | 1750 | + | + | + | + |
| Fenthion | S | 1500 | + | + | + | + |
| Mevinphos | T | 1000 | + | + | + | + |
| Phorate | R | 500 | + | + | + | + |
| Ronnel | R | 1250 | + | + | + | + |

[a] Identifies components of pesticide mixtures.
[b] + = stable.

### *Preparation, Storage, and Stability Testing of Acetone Formulation Solutions*

*Organochlorines and organophosphates.*—On the first day of the experiment, stock solutions were prepared in benzene as previously mentioned. Dilute mixtures were then prepared in acetone at concentrations 10 times that normally used for GC injections (Table 3). These mixtures were subdivided into 2 different storage containers for solvent evaporation comparison: 6 sealed glass ampules (one per month of the study) and a prescription bottle. All samples were stored at −15°C when not in use. Solutions from both container types were monitored monthly. Acetone mixtures were diluted 1:10 with isooctane just before GC quantitation. (A study conducted at the beginning of the experiment indicated that the detector response was not affected by the presence of 10% acetone in isooctane.) The electron capture detector was used for organochlorines; organophosphates were analyzed with the Tracor 222 equipped with a flame photometric detector (P mode).

Because this acetone study was initiated after completion of the GC working reference standard solution study, the reference solutions of organochlorines and organophosphates were known to be stable for up to one year when stored in the freezer at −15°C. Reference standards for this study were, therefore, prepared at injection concentration as isooctane dilutions of the reference stock solutions and stored in the freezer.

## Results and Discussion

By the criterion that decomposition of less than 10% over the length of the study is defined as stable, 59 of 70 compounds tested proved to be stable in the working solution study. Eight compounds were unstable only at ambient temperature and 3 other compounds were unstable under all storage conditions. All of the 13 organochlorines and 10 organophosphates tested in the acetone formulation solution study proved to be stable in the freezer by this criterion.

### *Working Standards Stability Experiment*

*Organochlorines (in Isooctane).*—All compounds

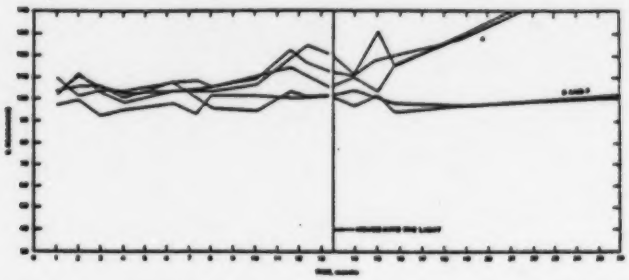

**Figure 1. Degradation curves of DDT-type compounds from working standard study (isooctane, ambient temperature). Degradation curves from solution A (*p,p'*-DDT, *p,p'*-DDE, and *o,p'*-DDT) illustrate solution concentration by solvent evaporation. B = *p,p'*-DDD; F = methoxychlor.**

in this class (24 single component compounds, plus toxaphene, chlordane, and Aroclors 1016 and 1254) were stable in isooctane under test conditions during the 2 years of study (Table 1). The compounds were stable to chemical degradation even under the most severe test conditions. As illustrated in Figures 1 and 2, the stability data plots of the DDT-type compounds and the Aroclors do not indicate any reduction of concentration. The 3 compounds from solution A increased in concentration after month 10, obviously due to solvent evaporation because only two-thirds of the solvent was left at the end of 2 years. The other 2 compounds are of the same general chemical structure (*p,p'*-DDD and methoxychlor), but were in mixtures B and F that did not exhibit concentration through solvent evaporation.

Only a few of the compounds could be illustrated, but they are typical of all of the other compounds tested.

*Organophosphates (in Isooctane).*—All compounds in this class (20 compounds) except disulfoton showed no degradation in isooctane during 2 years under all test conditions (Table 1; Figures 3 and 4). The degradation of disulfoton was evident under all storage conditions (Figure 4). The results illustrated, with the exception of disulfoton, are typical of the remaining organophosphates tested.

*Carbamates (in Toluene).*—Only 8 of the 13 test compounds in this class were stable in toluene under all 4 test conditions (Table 2). CDEC (in isooctane) and butylate decomposed rapidly under all test conditions (Figure 5). Butylate decomposed approximately 50% per year under all test conditions. CDEC decomposed 50–98% per year depending on storage conditions.

Carbaryl, carbofuran, and methiocarb decomposed 38, 17, and 40%, respectively, with exposure to light at ambient laboratory temperature in one year. Of these, only methiocarb was unstable (13% decomposition) during the same time period at ambient temperature when stored in the dark. Solutions of aminocarb, thiobencarb, mecarbam, bufencarb, mexacarbate, pirmicarb, promecarb, and propoxur were stable for one year under all conditions tested. Representative examples of some of the ambient-dark degradation curves are given in Figure 6.

*Triazines (in Ethyl Acetate).*—Only half the compounds tested in this group were stable

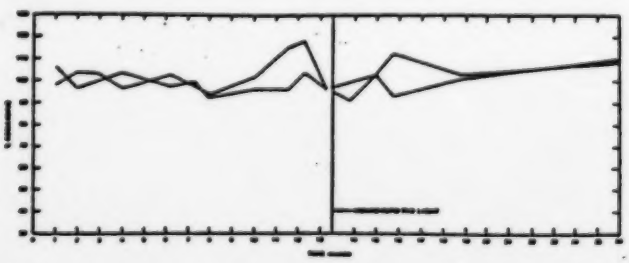

**Figure 2. Degradation curves of Aroclors 1016 and 1254 from working standard study (isooctane, ambient temperature).**

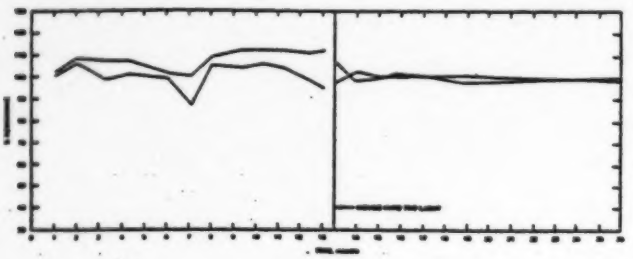

Figure 3. Degradation curves of ethyl and methyl parathion from working standard study (isooctane, ambient temperature).

under all test conditions (Table 2). Figures 7 and 8 are representative of the stability curves of some stable compounds: chlorine-, methoxy-, and thiomethyl-substituted compounds.

Atrazine and atraton degraded approximately 15% in one year at ambient temperature in the dark. Prometryn, prometon, atrazine, and ametryn degraded 11–17% at ambient temperature with exposure to light. Because of solvent evaporation from the atraton solution container, decomposition of atraton with light exposure could not be measured.

### *Acetone Formulations of Organochlorines and Organophosphates*

All 19 individual compounds and 3 technical mixtures (chlordane and Aroclors 1016 and 1254) in acetone were stable at −15°C to chemical degradation for the 6 months of the test (Table 3) and would be suitable for preparation of quality assurance samples. No evaporation was evident in either the ampule or the screw-cap prescription bottle.

### *Degradation Curve*

Because of the extent of chemical breakdown of disulfoton, CDEC, and butylate, their data were used as models for regression analysis. The regression correlation coefficients for the first order rate equation

$$\ln \frac{C_0}{C} = kt, \quad \text{or} \frac{C}{C_0} = e^{-kt}$$

were high (>95% confidence), indicating that degradation of these compounds was at least pseudo-first order. The calculated time necessary for 10% decomposition of the unstable compounds is listed in Table 4.

Degradation rate curves show exponential decreases in concentration. The most severe changes, therefore, occur early in the life of the standard solution. General recommendations reflect this fact and consequently may appear more conservative than a cursory review of results would indicate.

## Conclusions and Recommendations

The majority of compounds proved to be stable (less than 10% concentration change) in organic solution for one year when stored under any of the 4 test conditions. Therefore, standard solutions of these stable compounds can be used for one year for accurate quantitative determinations as long as solvent evaporation is properly con-

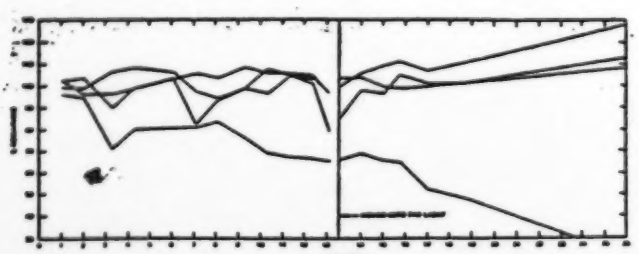

Figure 4. Degradation curves of organophosphates containing thio-ether functions from working standard study (isooctane, ambient temperature). Compounds include phencapton, fenthion, carbophenothion, and disulfoton; disulfoton (A) illustrates significant degradation.

Table 4. Time (in months) for 10% degradation of unstable compounds under test conditions

| Compound | Conditions | | | |
|---|---|---|---|---|
| | Freezer −15°C | Refrig. +3°C | Dark ~24°C | Light ~24°C |
| Organophosphates (in isooctane) | | | | |
| Disulfoton | 2.18 | —[a] | 3.27 | 1.18 |
| Carbamates (in toluene) | | | | |
| Butylate | 2.02 | 1.90 | 1.91 | 1.93 |
| Carbaryl | — | — | — | 2.55 |
| Carbofuran | — | — | — | 7.58 |
| CDEC | 1.31 | 1.54 | 2.13 | 0.368 |
| Methiocarb | — | — | 10.2 | 2.70 |
| Triazines (in ethyl acetate) | | | | |
| Ametryn | — | — | — | 7.21 |
| Atraton | — | — | 8.93 | —[b] |
| Atrazine | — | — | 2.17 | 9.66 |
| Prometon | — | — | — | 11.3 |
| Prometryn | — | — | — | 11.7 |

[a] <10% degradation.
[b] Reference to discussion, this solution concentrated.

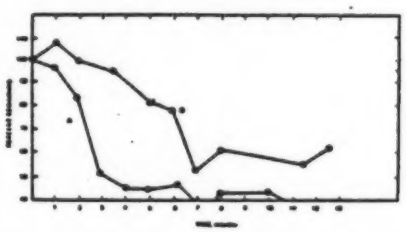

Figure 5. Degradation curves of CDEC in isooctane (A) and butylate in toluene (B) from working standard study (ambient temperature in the dark)

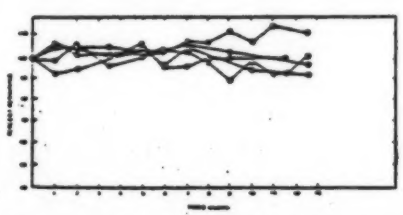

Figure 6. Degradation curves of 5 aromatic *N*-methyl carbamates from working standard study (toluene, ambient temperature in the dark). Compounds include propoxur, carbofuran, methiocarb, carbaryl, and aminocarb.

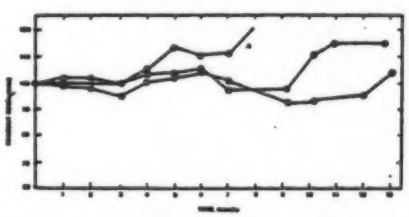

Figure 7. Degradation curves of triazines containing chlorine on the ring from working standard study (toluene, ambient temperature in the dark). Compounds include simazine, cyanazine, and propazine. Simazine (A) illustrates solvent evaporation after month 4.

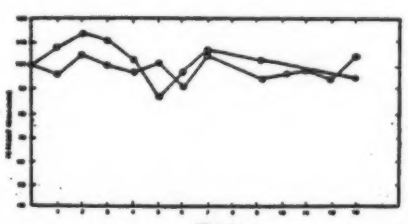

Figure 8. Degradation curves of triazines containing $-OCH_3$ and $-SCH_3$ on the ring from working standard study (toluene, ambient temperature in the dark). Compounds include ametryn and atraton.

trolled through use of recommended solvents, storage vessels, storage conditions, and solvent volume monitoring (see Part I, ref. 3). Acetone solutions of organochlorine and organophosphate pesticides were also useful for at least 6 months.

Quality control practices recommended from the stability study results are as follows:

(1) Primary reference standards: Store in a desiccated container in the freezer.

(2) Concentrated stock solutions: Store in a freezer. Every year, replace compounds that did

not degrade (Tables 1 and 2). Every 6 months, replace compounds that degrade only at ambient temperature. This group includes carbaryl, carbofuran, methiocarb, ametryn, atraton, atrazine, prometon, and prometryn. Monthly, replace compounds that degraded under all test conditions. This group includes disulfoton, CDEC, and butylate. Other alkyl carbamates that were not tested, such as vernolate, pebulate, etc., should probably also be in this group.

(3) Dilute working solutions: Store stable compounds (Tables 1 and 2) in a refrigerator if not in daily use. Replace by dilution from stock solution every 6 months. If solutions were used often and left on bench top, replace by dilution from stock solution every 3 months. Replace sooner if evaporation is evident. Compounds known to be unstable at ambient temperature should be stored in a refrigerator between uses and be replaced with fresh dilutions from stock solutions every 2 months. Replace sooner if evaporation is evident. Unstable compounds should be stored in a refrigerator between uses and be replaced with fresh dilutions from stock solutions every week.

## Acknowledgments

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